Optical Properties of Polyvinyl Chloride Doped with DCM dye Thin Films

Ahmed Namah Mohamed\textsuperscript{1},* Akeel Shaker Tuhaiwer\textsuperscript{1}, Zaid Saud Razzaq\textsuperscript{2}

\textsuperscript{1}Physics Department, College of Science, Muthanna University, Al-Muthanna, Samawa, Iraq
\textsuperscript{2}Department of Science, College of Basic Education, Muthanna University, Al-Muthanna, Samawa, Iraq

*E-mail address: aljeashie@gmail.com

ABSTRACT

Optical properties such as absorption coefficients, refractive indices, and extinction coefficients of pure polyvinyl-chloride (PVC) and DCM laser dye doped with PVC thin films where prepared using casting method have been determined in the range between 190-1100nm. Measurement have been performed in pure and doped (PVC). The direct electronic transition and indirect energy gaps were calculated using the behavior of absorption coefficient with wavelength. The direct energy gap was 3.9e.V for pure PVC and 2e.V for doped PVC, but indirect energy gap was 2.4e.V for pure PVC and 1.1e.V for doped. The phonon energy was 1.05e.V for pure PVC and was 0.55e.V for DCM doped with PVC thin film.

Keywords: polyvinyl chloride, DCM, optical properties, thin films

1. INTRODUCTION

The doped material and precipitated as thin films is one of the appropriate technique to study many of the physical and chemical properties that are difficult to obtain when the
material in natural form [1]. The term thin-film using to describe a single or several layers of the material atoms does not exceed a thickness one macron [2].

Thin films have special and import properties can be used in scientific and industrial fields [3]. There are number of materials which have been used as solid hosts for laser dyes such as: polymers, porous glasses, organically modified silicates or silicate nanocomposites, and polycom glass (combination of polymer and sol–gel) [4].

Some important characteristics gave polymers forefront to be a host for dyes which possess many favorable optical properties in comparison with other types of solid hosts. The high homogeneity of polymers is important for narrow line width oscillators, and one can quit efficiency control the chemical composition at the formation stage, and the show much better compatibility with organic laser dye [5].

Incorporating laser dyes in polymer hosts decreases the degradation the dye, the stability of the dye increases and the fluorescence intensity increases as well. This is due to the dimmers decomposition which terminates the absorption process that accrues in the same region of fluorescence resulting from re-absorption [6].

![Figure 1. Structural formula of DCM laser dye.](image1)

![Figure 2. Structural formula of PVC [8].](image2)
A laser dye used in this study was DCM laser dye, structural formula is shown in figure (1). Synonym: [2-[2-[4-(dimethylamino)phenyl]ethenyl]-6-methyl-4H- pyran-4-ylidene]-propanedinitrile and the chemical formula is C_{19}H_{17}N_{3}O_{7}.

This laser dye mixed with PVC with structural formula shown in Figure (2), with chemical formula (C_{2}H_{3}Cl)_{n}.

2. EXPERIMENTAL PART

2.1. Sample preparation

Polyvinyl chloride was used as a host polymeric material in this work, supplied by (BDH chemicals) with high purity, the aqueous solution of this polymer were prepared by dissolving 1 gm of PVC in 30ml THF and thoroughly stirred using a magnetic stirrer for about one hour until PVC was completely dissolved.

Preparation the desired concentration of the dye by weighting the right amount of dye using the equation [9]

\[ W = \frac{M_w \times V \times C}{1000} \]  

where: W weight of the dissolved dye (g)
M_w Molecular weight of the dye (g/ml)
V the volume of the solvent (ml)
C the dye concentration (ml/lit)

To prepare 5×10^{-3} mol/lit DCM dye solution, firstly dissolving 0.015 gm in 10 ml of THF to obtain 10 ml of dye solution.

Mixing 5ml of PVC solution with 5ml of dye solution and stirrer about 20 minutes to obtain homogenous solution. This mixture casting on glass substrate at room temperature and atmospheric pressure to obtain the final thin films.

2.2. Thin films thickness measurement

Thickness of the prepared thin films was measured using the optical interferometer method employing He-Ne laser 0.632 μm with incident angle 45° as shown in Fig. (3)

This method depends on the interference of the laser beam reflected from thin film surface and then substrate, the films thickness (d) can be calculated using the following formula [10]:

\[ d = \frac{\lambda}{2} \cdot \frac{\Delta X}{X} \]  

-47-
2. 3. Optical properties measurements

The optical absorption spectra of pure PVC and DCM doped with PVC thin films were recorded at room temperature using UV-VIS double beam spectrometer in the wave length range from 190 to 1100 nm.

The optical absorption coefficient ($\alpha$) of pure PVC and DCM doped with PVC films is very important because it provides information on the electronic band structure. This coefficient was calculated using the following relation [11]:

$$\alpha = \frac{2.303}{d} A$$  \hspace{1cm} (3)

The reflectance was calculated after determined the transmittance ($T$) from the UV-VIS spectrometer using the following formula [12]

$$A + T + R = 1$$  \hspace{1cm} (4)

and the linear refractive index ($n$) is given by [13]
\[ n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (5) \]

The extinction coefficient is obtained in terms of the absorption coefficient using the following formula [14]

\[ K = \frac{\alpha \lambda}{4\pi} \quad (6) \]

3. RESULTS AND DISCUSSION

Figure (4) shows the optical absorption spectrum of pure PVC thin film sample. In the UV region, the absorption decreases with increasing the wavelength which is related to high energy absorption. While in the visible region there are no absorption bands since the films are transparent, and the absorbance will be constant in this region.

![Absorption spectra of pure PVC and DCM doped with PVC thin films](image)

**Figure 4.** Absorption spectra of pure PVC and DCM doped with PVC thin films

But when the PVC doped with DCM laser dye the absorption spectrum shifted to a higher wavelength in the visible region as shown in Figure (4). The absorbance intensity increases with a little shifting towards higher wavelengths, these agree with beer-Lambert law.
Figure (5) illustrates the dependence of the liner absorption coefficients on the photon wavelength for pure PVC thin film and PVC doped with DCM, where their values increase rapidly beyond absorption edge regions for the two samples (pure and doped PVC).

**Figure 5.** Absorption liner coefficient of pure PVC and DCM doped with PVC thin films.

**Figure 5.** Absorption liner coefficient of pure PVC and DCM doped with PVC thin films
From the shape of the \( (\alpha > 10^4 \text{ cm}^{-1}) \), one can deduce the transfer represents the electronic direct transfer \([15]\). Based on this result has been drawing the relationship between the values of \((\alpha h \nu)^2\) as a function of energy is a straight line tangent to the curve is determined by the values of the direct energy gap \([16]\). These energy gap values was calculated from Figure (6) for pure PVC thin film and from Figure (7) for DCM doped with PVC's.

![Figure 6. Dependence of \((\alpha h \nu)^2\) on the photon energy for pure PVC thin film](image6)

The direct electronical transition energy gap was 3.9e.V for pure PVC thin film, while this energy was 2e.V for DCM doped with PVC thin film.

![Figure 7. Dependence of \((\alpha h \nu)^2\) on the photon energy for DCM doped with PVC thin film](image7)
Figure (8) shows the relation between $(\alpha h\nu)^{1/2}$ and photon energy for pure PVC thin film. It has been observed from this figure that the indirect electronic energy gap; $E_g = 2.4\text{e.V}$ and the phonon energy; $E_p = 1.1\text{e.V}$.

![Figure 8](image)

**Figure 8.** Dependence of $(\alpha h\nu)^{1/2}$ on the photon energy for pure PVC thin film

Figure (9) shows the dependence of $(\alpha h\nu)^{1/2}$ and photon energy for DCM doped with PVC thin film. It has been observed from this figure that the indirect electronic energy gap; $E_g = 1.05\text{e.V}$ and the phonon energy; $E_p = 0.55\text{e.V}$.

![Figure 9](image)

**Figure 9.** Dependence of $(\alpha h\nu)^{1/2}$ on the photon energy for DCM doped with PVC thin film
Figure 10. Refractive index variation with the wavelength for pure PVC thin film

Figure 11. Refractive index variation with the wavelength for DCM doped with PVC thin film
Figure 12. Extinction coefficient of pure PVC thin film variation with the wavelength

Figure 13. Extinction coefficient of DCM doped with PVC thin film variation with the wavelength
Figure (10) shows the variation of refractive index of thin film consist of casting PVC polymer. As shown from this figure, the refractive index decreases as the wavelength increase until 400 nm and then become nearly constant with increasing wavelength; the value of refractive index within the constant range was varying from 1.42-1.75.

On the other hand the refractive index of the thin film composed of DCM doped with PVC polymer shown in Fig. (11). It is obviously that the refractive index of the thin film initially decreasing to the lowest value at 559 nm after that it increases readily at 562 nm then the refractive index clears to be constant with increasing the photon energy.

The extinction coefficient allows for estimation the molar concentration of the mixture before casting the solution on the glass substrate. Figure (12) shows the plot between the extinction coefficient against the wavelength of the pure PVC thin film. The extinction coefficient decreasing with increasing the photon energy, then it is increasing beyond 400 nm wavelength. Figure (13) shows the variation of the extinction coefficient with the wavelengths of the DCM doped with PVC thin film. It is undergoing a shifting toward the longer wavelength.

4. CONCLUSIONS

In the current work, the optical properties of the prepared thin films shows that the red shifting in absorption spectrum of dopant film caused by the doping while inverse occurs in linear absorption coefficient. From the linear absorption spectra on can deduce that the direct electronic transition energy gap decreasing from 3.9 e.V for pure PVC thin film to 2 e.V in dopant thin film. The same thing happens for in direct electronic transition where $E_{g} = 2.4$ e.V for pure PVC and decreasing to be 1.1 e.V for dopant PVC. The phonon energy in indirect transition was 1.05 e.V for pure PVC and equal to 0.55 e.V for DCM doped with PVC thin film.

Acknowledgement

Author(s) would like to express him (their) thanks to Dr. Jafer Fahdel Odah to his helped and supported him (their) during the period of preparing this work.

References


(Received 07 November 2015; accepted 19 November 2015)